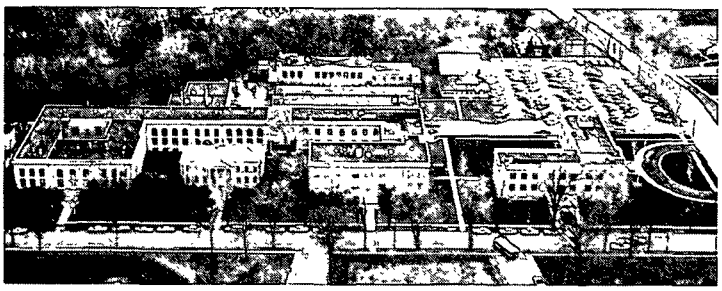

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ELECTRON-TRANSFER REACTIONS IN PULPING SYSTEMS (V): THE APPLICATION OF AN INTRAMOLECULAR CYCLIZATION REACTION AS A DETECTOR OF ELECTRON-TRANSFER TO QUINONEMETHIDES

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ELECTRON-TRANSFER REACTIONS IN PULPING SYSTEMS (V): THE APPLICATION OF AN INTRAMOLECULAR CYCLIZATION REACTION AS A DETECTOR OF ELECTRON-TRANSFER TO QUINONEMETHIDES

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ABSTRACT

An electron-transfer probe compound which incorporates a hex-5-enyl group on a quinonemethide precursor has been synthesized and reacted in 1M NaOH at 135°C in the presence of various pulping additives. Reduction of the probe compound either prior to or after cyclization to a 5-membered ring provides evidence for radical intermediates and electron-transfer processes. Some additives such as anthrahydroquinone and glucose were effective electron-transfer agents to the probe quinonemethide, while others such as sodium sulfide and sulfite were ineffective. The probe, therefore, provides information on the nature of chemical reactions which may be occurring during the pulping of wood.

Anthrahydroquinone and glucose provided significantly different amounts of cyclized products. Glucose gave high yields of cyclized products, including three unique tricyclo-[7.3.0.$0^{2,7}$]-dodecatrienes. Apparently glucose reduces the radical intermediates relatively slowly, providing time for cyclization to occur. With no additives other than 1M NaOH, and long reaction times, the probe compound provided some cyclized products; the electron-transfer agent in this case presumably is a phenolate ion.

INTRODUCTION

Wood is composed of two principal materials, carbohydrates and lignin. The goal of the alkaline pulping of wood is to remove the

lignin and retain the carbohydrates. Lignin removal is accomplished by the fragmentation of the lignin polymer into water soluble particles. To aid the delignification process, pulping additives such as sodium sulfide, sodium sulfite, and anthraquinone are used. Anthraquinone (AQ) as an additive is a rather recent discovery, and much interest has been generated in its mechanism of action.[1]

Studies investigating the beneficial effects of anthraquinone indicate that it aids pulping by oxidizing the aldehyde end groups of the carbohydrates to alkali-stable acid groups.[1] During this process, the yield of pulp increases and anthraquinone is reduced to anthrahydroquinone (AHQ). Anthrahydroquinone is able to fragment lignin by a reductive process, which regenerates anthraquinone.[1] The latter reaction contributes to the rapid rates of delignification associated with anthraquinone pulping. Thus, a cyclic redox mechanism is established (Fig. 1).

Fragmentation of lignin model compounds by AHQ has been extensively studied.[2-5] One proposed mechanism for an AHQ induced lignin fragmentation process is that AHQ^{-2} adds to a quinonemethide (QM), forming a QM-AHQ^{-2} **adduct** which subsequently undergoes an elimination reaction producing fragmented products and AQ. Simple adducts of model compounds have been prepared and shown to exhibit this kind of chemistry.[2-5] However, since adduct formation reactions are reversible,[6] it is not clear whether adducts are key intermediates to fragmentation or just part of side reactions.

An alternative mechanism for an AHQ induced lignin fragmentation process is one involving reduction of quinonemethides by AHQ ions **via** electron transfer processes (Scheme 1). The requirement of electron-poor and electron-rich substrates, necessary for electron-transfer, is met with a QM and AHQ ions, respectively. Quinonemethides in pulping systems are generated when lignin or models of lignin which are phenolic and having leaving groups at the <u>para</u> α-carbon are heated, i.e., **1** —> **2**. The QM **2** shown in Scheme 1 contains a labile C_β-aryl ether bond; such bonds contribute 50-60% of interunit linkages in lignin.[7] The "A" units on

the structures in Scheme 1 represents the aromatic ring or quinonemethide unit in a terminal monomer unit of lignin; "B" is the aromatic ring in the second monomer in the chain.

Fragmentation of lignin by electron transfer (Scheme 1) is viewed as beginning with a transfer of an electron from AHQ^{-2} to a QM, producing $AHQ^{\cdot-}$ and a quinonemethide radical anion ($2^{\cdot-}$). The ($QM^{\cdot-}$) then fragments to a phenolate ion and a phenoxy radical; a second electron-transfer converts the phenolate radical to a phenolate ion. The two proposed phenolate ion products, 3 and 4, are the same ones observed when QM-AHQ adducts are heated in alkali.[2-5]

Evidence supporting an electron-transfer fragmentation process (Scheme 1) has been provided by observing the cleavage of a relatively stable β-aryl ether QM in the presence of electrochemically generated $AHQ^{\cdot-}$.[9] The study, however, employed conditions quite different from pulping; the temperature was ambient and the solvents were principally organic.

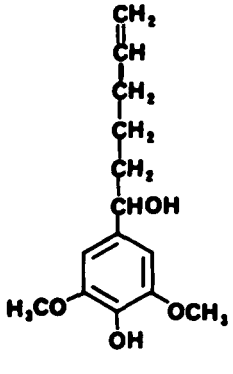
Studies aimed at defining the exact nature of the QM/AHQ interaction have been hampered by the fact that formation of the QM species is the rate determining step for fragmentation.[9-12] The use of clock reactions, however, has demonstrated that AHQ is superior to other reagents at causing β-aryl ether cleavage,[13] implying that its chemistry is different than the usually accepted adduct chemistry exhibited by other additives.

In order to determine if certain reagents can electron-transfer to lignin model quinonemethides under conditions similar to alkaline pulping (1M NaOH and 170°C), we have synthesized and studied the alkaline reactions of a compound which is soluble in alkali, can form a QM, and can show the existence of a radical intermediate. The reaction of the compound with chemicals typically present during pulping, such as AHQ, carbohydrates, sulfite and sulfide, is the subject of this report.

RESULTS

Cyclization of hex-5-enyls to five-membered rings is generally assumed to be diagnostic of the intermediacy of radicals in reaction mechanisms.[14,15] A compound containing a hex-5-enyl group and substituents necessary for QM formation, namely a free phenol and a leaving group at the α-carbon of a para-side chain, was sought to determine if electron-transfer to QMs is possible under pulping-like conditions. Model compound 5, which meets the desired criteria, was easily prepared by the Grignard reaction of 5-bromo-1-pentene with syringaldehyde. Unfortunately, the alkaline reactions of 5 at 135°C resulted in only dehydration, yielding styrene products; even addition of AHQ did not prevent dehydration.

A second model (6) was prepared with methyl groups at the β-position. Besides blocking dehydration, these methyl groups have the additional benefit of increasing the rate of cyclization.[16] Synthesis of 6 was accomplished by converting 5-chloro-5-methyl-1-hexene to a Grignard reagent and mixing the latter with syringaldehyde. The expected reactions of 6 are shown in Scheme 2.



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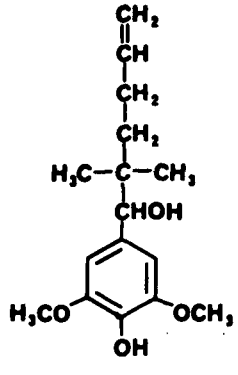


6

NaOH Reactions

The reaction of 6 in 1M NaOH at 135°C for four hours provided only low yields of 2,6-dimethoxyphenol (syringol). Syringol was always observed as a product when 6 was reacted in hot alkali. The mechanism of formation of syringol probably involves a reverse aldol reaction from a keto form of the phenol 6; its formation

does not appear to be related to electron-transfer. When the reaction time was increased to 18 hours, small yields of cyclized compounds **10**, **13**, and **14** were observed (Fig. 2). Scheme 3 shows compounds **13** and **14**, and a possible route to their production.

Anthrahydroquinone Reactions

When two equivalents of AHQ were present during the heating of **6** at 135°C in aqueous alkali, two products (**8** and **10**) were observed in good yields in less than two hours (Fig. 2). In contrast to the NaOH reaction, very little starting material remained after 2 hours. The major product in the AHQ reaction was the acyclic compound **8**; the simple cyclized compound **10** was only present in small amounts and the more extended cyclized compounds **12-14** were absent.

Other Pulping Reagents

Two other compounds used to aid delignification, sodium sulfide and sodium sulfite, were also tested for their ability to transfer electrons to the quinonemethide derived from **6**. Both these inorganics did not provide any increase in cyclized products as compared to the reaction of **6** with no additives. Even at 170°C, sulfide displayed no ability to electron-transfer. The inability of sulfide to transfer electrons is in agreement with past research[17] and other recent studies.[18]

Carbohydrate Reactions

Both soluble and insoluble carbohydrates are present during the pulping of wood. Some of these carbohydrates have "reducing end groups." Even though the lifetime of a reducing sugar is extremely short at 120-170°C,[19] these structures may be a source of electrons for reducing quinonemethides. Fullerton and Wilkins have shown that the fragmentation of β-aryl ether lignin models is promoted by reducing sugars.[20] Quinonemethide-carbohydrate adducts were synthesized and found to fragment an internal β-aryl

ether linkage under pulping-like conditions; an ionic mechanism of fragmentation *via* an adduct intermediate was proposed. Yet, as in AHQ induced model fragmentation, the adduct may not be part of the reaction sequence which leads to cleavage.

As shown in Fig. 2, the addition of five molar equivalents of glucose to an alkaline reaction of **6** provided cyclized compound **10** as the major product. Also formed were the acyclic compound **8**, and the cyclic compounds **12**, **13**, and **14**. When compared to AHQ addition, the yield of **8** was greatly decreased, while the yields of cyclized compounds **10**, and **12-14** were substantially increased.

A further study into the ability of carbohydrates to electron-transfer involved a determination of the necessity of the free aldehyde ("reducing" end) for electron transfer. Both methyl α- and β-D-glucopyranoside are nonreducing sugars and, when compared to glucose, both gave much less cyclized products. With methyl-α-D-glucopyranoside, roughly a 75% yield of starting material and a 15% yield of cyclized products were present after 18 hours reaction time at 135°C. For the β-isomer, 54% starting material and 36% cyclized products were observed after reaction for 18 hours. The greater reactivity of the β-derivative is in accord with its faster degradation rate (to a reducing sugar) in aqueous alkali.[21] It is apparent that a free aldehyde is necessary for good electron transfer.

Product Characterization

Column chromatography was employed to isolate a small sample of acyclic product **8** from the AHQ reaction of **6** (Fig. 2); the sample was readily characterized by spectral means. Likewise, small samples of cyclized products **10** and **12-14** were isolated and characterized.

Table 1 presents the ^{13}C-NMR data for **6** and its reaction products. The data clearly support the structural assignments; ^{1}H-NMR and MS data lend additional support (see Experimental Section). Distinguishing spectral features for cyclized products

10 and 12-14 are the lack of olefinic carbons and a corresponding increase in aliphatic carbons. The symmetry of the aryl rings for 6 and 8 is apparent from the spectra. The number and position of the aryl-CH carbons differentiates compounds 12-14; the two upfield aryl-CH carbons in 13 indicate two protons ortho to oxygen aryl substituents, while 14 has only one of this type. The difference in the number of methoxyl groups in compounds 13 and 14 is also distinguishing.

Table 1. The ^{13}C-NMR data for 6 and the products formed from the reaction of 6 in 1M NaOH at 135°C.[a]

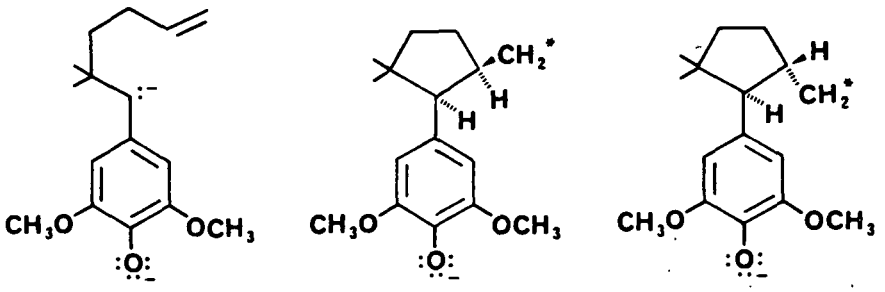
Compound	6	8	10	12	13	14
Carbon						
C_1	81.0[c] (d)	48.3 (t)	64.8 (d)	61.5 (d)	61.5 (d)	59.7(d)
C_2	--[b]	34.1 (s)	42.4 (s)	44.8 (s)	--[b]	--[b]
C_3	38.0 (t)	28.7 (t)	40.5 (t)	38.1 (t)	40.9 (t)	38.5 (t)
C_4	28.4 (t)	40.8 (t)	31.0 (t)	32.2 (t)	32.3 (t)	32.2 (t)
C_5	139.2 (d)	139.2 (d)	37.4 (d)	43.6 (d)	43.8 (d)	43.9 (d)
C_6	113.6 (t)	113.6 (t)	19.6 (q)	42.6 (t)	42.6 (t)	42.5 (t)
gem-	22.9 (q)	26.9[c](q)	24.5 (q)	24.9 (q)	25.2 (q)	24.9 (q)
di-Me	23.0 (q)		29.4 (q)	30.1 (q)	30.2 (q)	29.9 (q)
C_1'	133.6 (s)	133.7 (s)	133.0 (s)	136.4 (s)	127.1 (s)	134.6 (s)
C_2'	104.5 (d)	107.2 (d)	105.9 (d)	128.0 (s)	144.5 (s)	137.8 (s)
C_3'	146.0 (s)	146.1 (s)	146.3 (s)	146.3 (s)	109.9 (d)	142.2 (s)
C_4'	132.9 (s)	132.8 (s)	131.6 (s)	135.5 (s)	145.0 (s)	146.4 (s)
C_5'	146.01 (s)	146.1 (s)	146.3 (s)	142.4 (s)	135.6 (s)	113.2 (d)
C_6'	104.5 (d)	107.2 (d)	105.9 (d)	103.6 (d)	107.8 (d)	120.5 (d)
OCH_3	56.2[c](q)	56.2[c](q)	56.2[c](q)	56.4 (q)	56.3 (q)	60.6 (q)
				59.7 (q)		

[a]The numbering system begins with the benzyl carbon as 1 and its attachment to the ring at the 1' carbon.
[b]Not observed.
[c]Represents two methyls (strong peak).

DISCUSSION AND CONCLUSIONS

The production of cyclization products from high temperature reactions of compound 6 indicates that electrons have been transferred to the quinonemethides intermediate produced from 6. This

transfer is most likely of the singlet electron transfer (SET) type (Schemes 2 and 3). A two electron transfer, either as a single step or two SET steps, would have to generate a dianion 7^{-2}. The latter should be a high energy species and therefore probably would not readily form in aqueous alkaline solutions, even at high temperatures. It is difficult to rationalize the production of a carbanion species (7^{-2}) from a phenolate ion species (AHQ^{-2}).



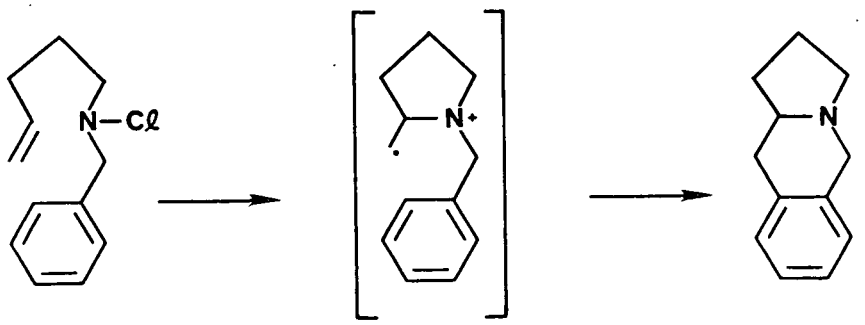
7^{-2} $\quad$ $9a^{\dot{-}}, \bullet = \bullet$ $\quad$ $9b^{\dot{-}}, \bullet = \bullet$

$15a^{-2}, \bullet = :^-$ $\quad$ $15b^{-2}, \bullet = :^-$

Cyclization of radicals is reported to occur with high cis-stereospecificity,[22] meaning that $9a^{\dot{-}}$ should form in preference to $9b^{\dot{-}}$. In contrast, carbanion cyclizations, if they occur, reportedly give a predominance of trans-sterospecificity during cyclization,[23] meaning that $15b^{-2}$ should be favored over $15a^{-2}$. Thus, knowing the stereochemistry of cyclized product **10** would indicate the nature of its precursor intermediate, either $7^{\dot{-}}$ or 7^{-2}. Unfortunately, due to overlapping of NMR signals, the coupling constant of the benzylic proton (which would help define the stereochemistry) could not be obtained for compound **10**.

Because of strain effects, the geometry about the C_α and C_δ carbons of cyclized products **12-14** must be cis. Significant amounts (Fig. 2) of **12-14** are produced from the reaction of **6** with glucose, meaning some, and possibly all of the cyclized products in this reaction have cis-stereochemistry, and SET reactions prevailed.

Scheme 3 presents a probable reaction sequence for the formation of the additional cyclized products (12-14). There is precedence for two successive radical cyclizations involving an olefinic double bond and an aromatic ring, namely the conversion of 16 to 18 by way of intermediate 17.[24]



16 17 18

The probe compound 6 thus provides a means to test the possible existence of electron-transfer reactions under different pulping conditions. Because of the bulk and nature of the substituents, the quinonemethide 7 may be stable in aprotic solvents.[25,26] Thus, 7 prepared from 6 in a solvent like chloroform[25] could serve as a general detector of electron-transfer reactions.

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer Model 700 infrared spectrometer and standardized with polystyrene. A Jeol FX 100 spectrometer was used to obtain the NMR spectra. The mass spectra were obtained with a Hewlett Packard Model 5985 GC-MS spectrometer using a six foot 3% silicone OV-17 on 100/120 chromosorb W-HP MAOT-350 column.

Syringaldehyde and 4-bromo-1-butene were obtained from Aldrich Chemical Co., Milwaukee, Wisconsin, while 1-bromo-4-pentene was obtained from ICN Pharmaceuticals, Inc., K & K Laboratories, Plainview, New York. Ultrapure NaOH was obtained as a 30% solution from Alfa Products, Danvers, Massachusetts. Silica gel 60 (70-230 mesh ASTM) was used in all chromatographic separations.

Oxygen-free water was prepared by boiling distilled water for about 30 minutes, after which nitrogen was dispersed into the water as it cooled to room temperature. After cooling, the water was sealed under nitrogen until needed.

6-Hydroxy-6-(3',5'-dimethoxy-4'-hydroxyphenyl)-1-hexene (5).

To an oven-dried 500 mL three-necked round-bottom flask flushed with nitrogen was added 0.90 g (0.037 g atom) of magnesium turnings and enough anhydrous ether to cover the turnings. Connected to the flask was an oven-dried 250-mL pressure equalizing addition funnel containing a 150 mL anhydrous ether solution of 5.5 g (0.037 g mole) of 5-bromo-1-pentene. A constant flow of nitrogen was maintained through the apparatus as a few drops of 1,2-dibromoethane and about 10 mL of the ether solution were used to initiate the reaction. The remaining ether solution was added to the stirred contents of the flask at a rate that gently refluxed the ether. After the complete addition of the ether, the solution was refluxed for 90 min in a 40°C water bath. Then about 75 mL of freshly distilled tetrahydrofuran (THF) was added, and the water bath temperature was increased to 70°C. Syringaldehyde (2.80 g, 0.015 mole) dissolved in 40 mL of THF was dripped into the reaction vessel. An hour after the syringaldehyde addition was complete, the reaction was quenched with 5 mL of water followed by 2M H_2SO_4. The THF was separated, filtered, dried (anhydrous $MgSO_4$), and evaporated to give a yellow liquid. Analysis of the liquid by ^{1}H-NMR and GC/MS identified the product as the ketone of the title compound.

The ketone was reduced by dissolving the yellow liquid in 50 mL of ethanol and adding dropwise 50 mL of distilled water containing 1.5 g of $NaBH_4$. After stirring overnight, the reaction solution was filtered, quenched with 100 mL of saturated ammonium chloride, and neutralized with 0.5M H_2SO_4. The aqueous solution was extracted twice with 70 mL of chloroform. The chloroform was combined, dried (anhydrous Na_2SO_4), and evaporated to give a

greenish solid. This solid was recrystallized from toluene/35-60°C petroleum ether to yield 1.70 g of a colorless solid: m.p. 91-92°C; IR (mull) cm^{-1} 3150-3600 (Ph-OH and HCOH), 1615 (CH_2=CH-); ^{1}H-NMR ($CDCl_3$) δ 1.5 (m, 2, C4-H_2), 1.7 (m, 2, C3-H_2), 2.0 (m, 2, C5-H_2), 2.08 (s, 1, -CHO<u>H</u>-, exchangable with D_2O), 3.87 (s, 6, -OCH_3), 4.6 (m, 1, -C<u>H</u>OH-), 4.9-5.1 (m, 2, CH_2=), 5.56 (s, 1, Ph-OH, exchangable with D_2O), 5.56-6.01 (d of d of t, 1, J = 17, 10, and 6 Hz, =CH-), 6.55 (s, 2, aryl); ^{13}C-NMR ($CDCl_3$) ppm 25.1 (t, C4), 33.5 (t, C5), 38.4 (t, C3), 56.1 (q, OCH_3), 74.4 (d, C6), 102.4 (t, CH_2=), 114.3 (d, C2', C6'), 133.6 (s, C1'), 135.8 (s, C4'), 138.3 (d, =CH-), 146.6 (s, C3', C5'); MS <u>m/e</u> (%) 252 (41, M+), 183 (100), 155 (47), 140 (30), 123 (95), 95 (57), 77 (32), 41 (53).

5,5-Dimethyl-6-hydroxy-6-(3',5'-dimethoxy-4'-hydroxyphenyl)-1-hexene (6).

Preparation of the Grignard reagent of 5-chloro-5-methyl-1-hexene proved difficult; refluxing ether resulted in the formation of undesired products. These undesired products were prevented by using large volumes of ether at room temperature. However, these conditions prevented the initiation and continuation of the Grignard reaction. To facilitate the reaction, periodic additions of methyl iodide were used to first initiate and then help maintain the reaction. Thus, by-products from methylmagnesium iodide were formed which had to be subsequently removed.

While in a nitrogen atmosphere, 1.0 g (0.0411 g atom) of magnesium turnings and 150-mL of anhydrous ether were added to an oven-dried 500-mL three-necked round-bottom flask. Added to two oven-dried 250-mL pressure equalizing addition funnels were 50-mL of anhydrous ether with 1.5 g (0.0113 mole) of 5-chloro-5-methyl-1-hexene[27] and 240 mL of anhydrous ether with 2.0 g (0.0141 mole) of methyl iodide, respectively. The glassware was assembled and approximately a fourth of the methyl iodide solution was added to the stirred turnings. When the reaction had started, the dropwise addition of the 5-chloro-5-methyl-1-hexene solution was begun.

This addition spanned 8-10 hours during which the methyl iodide solution was periodically added.

After the reaction solution had stirred overnight, silated syringaldehyde[28] dissolved in anhydrous ether was added dropwise until the brown color associated with the addition was no longer observed. The reaction was quenched with water followed by a small amount of 2M H_2SO_4. The entire solution was filtered (to remove unreacted Mg) and additional 2M H_2SO_4 was added. The acid (approximately 1M) and ether layers were allowed to sit together overnight to remove the silyl protecting group.

The ether layer was separated and extracted with a 1M NaOH solution to remove the phenolic products. A precipitate formed during this step. The precipitate, which was assumed to be the sodium salt of the desired product, was collected by filtration and redissolved in ether with the help of 0.25M sulfuric acid. Drying (Na_2SO_4), and evaporation of the ether solution gave a solid, which was recrystallized from hot toluene to give an off-white solid (**6**): m.p. 111-112.5°C; IR (mull) cm^{-1} 3150-3600 (OH's) and 1610 (CH_2=CH-); ^{1}H-NMR ($CDCl_3$) δ 0.86 and 0.93 (two s, 3 + 3, gem-dimethyls), 1.4 (m, 2, C4-H_2), 1.63 (broad s, 1, -CHOH-), 2.0 (m, 2, C3-H_2), 3.87 (s, 6, -OCH_3), 4.39 (s, 1, -CHOH-), 4.8-5.1 (m, 2, CH_2=), 5.46 (s, 1, Ph-OH), 5.63-5.96 (d of d of t, 1, J = 17, 10, and 6 Hz, =CH-), 6.54 (s, 2, aryl); shaking the NMR solution with two drops of D_2O removed the hydroxyl proton signals; ^{13}C-NMR ($CDCl_3$) ppm 22.9 and 23.0 (two q, gem-dimethyls), 28.4 (t, C4), 38.0 (t, C3), 56.2 (q, -OCH_3), 81.0 (d, -CHOH-), 104.5 (d, C2', C6'), 113.6 (t, CH_2=), 132.9 (s, C4'), 133.6 (s, C1'), 139.2 (d, =CH-), 146.0 (s, C3', C5'); MS m/e (%) 280 (7.1, M+), 183 (100.0), 155 (19.2), 140 (11.8), 123 (32.9), 95 (16.6), 55 (14.9).

Alkaline Reactions of 6. All reaction solutions of **6** were prepared in a nitrogen atmosphere with oxygen-free water and 30% ultrapure NaOH. The reactions were conducted in stainless steel

pressure vessels (bombs) of 4 mL capacity. Water and NaOH solution were added to make a 3.5 mL, 1M NaOH solution. The amount of **6** in each bomb was 0.0196 g (0.020 mole/liter).

The additives used were as follows: AHQ, as an AHQ-diacetate derivative,[29] (0.0412 g, 2 molar equivalents), glucose (0.0631 g, 5 molar equivalents), methyl α- and β-D-glucopyranoside (0.0680 g, 5 molar equivalents), Na_2S (0.0109 g, 2 molar equivalents), and Na_2SO_3 (0.0441 g, 5 molar equivalents). The bombs were sealed and tumbled in a 135°C oil bath for times ranging from 2 to 18 hours. After the desired length of time, the bombs were cooled in water. The contents of the bombs were neutralized with 2M H_2SO_4 and extracted with chloroform. Analysis of the chloroform solutions was by GC/MS.

Isolation and Characterization of Products

Isolation Procedures. Products **10**, **12**, **13**, and **14** were obtained from the reaction of **6** with 5 molar equivalents of glucose at 135°C in the previously described bombs. This procedure was repeated until 3.3 g of **6** were reacted. The contents of all the bombs were combined, neutralized with 5M H_2SO_4, and extracted with chloroform. The chloroform was dried (anhydrous Na_2SO_4) and evaporated. The solid was dissolved in a minimum amount of toluene, placed on a silica gel column, and eluted with toluene, with increasing amounts of ethyl acetate added to the toluene. Products **13** and **14** were separated, while products **10** and **12** were eluted together. Solutions containing **10** and **12** were evaporated, and the resulting liquid was placed on another silica gel column. Elution with petroleum ether (35-60°C) provided satisfactory separation.

Product **8** was obtained from the reaction of 0.8 g of **6** with 2 equivalents (1.2 g) of AHQ (prepared by the reduction of anthraquinone with $Na_2S_2O_4$) using a large reaction vessel (described in detail elsewhere[30]) and a temperature of 135°C. The final reaction

solution was neutralized with 5M H_2SO_4 and extracted with toluene. The toluene was dried (anhydrous Na_2SO_4) and evaporated. The solid was extracted with 35-60°C petroleum ether (done to remove products from the anthraquinone), which in turn was evaporated to a minimum volume, placed on a silica gel column, and eluted with 35-60°C petroleum ether. A good separation of **8** was obtained. Spectral data for products **8**, **10**, **12**, **13**, and **14** are presented below and in Table 1.

5,5-Dimethyl-6-(3',5'-dimethoxy-4'-hydroxyphenyl)-1-hexene (8).

IR cm^{-1} 1610 ($CH=CH_2$); ^{1}H-NMR ($CDCl_3$) δ 0.87 (s, 6, CH_3), 1.2-1.4 (m, 2, C4-H_2), 2.0-2.2 (m, 2, C3-H_2), 2.42 (s, 2, C6-H_2), 3.82 (s, 6, OCH_3), 4.7-5.1 (m, 2, CH_2=), 5.48 (broad s, 1, OH), 5.50-6.02 (d of d of t, 1, J = 17, 10, and 6 Hz, =CH-), 6.31 (s, 2, aryl); MS m/e (%) 264 (19.8, M+), 168 (40.6), 167 (100.0).

2-(3',5'-Dimethoxy-4'-hydroxyphenyl)-1,1,3-trimethyl-cyclopentane (10).

^{1}H-NMR ($CDCl_3$) δ 0.66 and 0.97 (two s, 3 + 3, gem-dimethyls), 0.93 (d, 3, J = 6 Hz, $-CH_3$), 0.8-2.3 (several m, C1-H, C3-H_2, C4-H_2, C5-H_1), 3.87 (s, 3, OCH_3), 5.39 (s, 1, OH), 6.35 (s, 2, aryl); MS m/e (%) 264 (81.4, M+), 168 (100.0), 167 (43.1).

12,12-Dimethyl-4,6-dimethoxy-5-hydroxy-tricyclo[7.3.0.0^{2,7}]-2,4,6-dodecatriene (12).

^{1}H-NMR ($CDCl_3$) δ 0.70 and 1.15 (two s, 3 + 3, gem-dimethyls), 0.8-3.2 (several m, C1-H, C3-H_2, C4-H_2, C5-H_1 C_6-H_2), 3.84 and 3.86 (two s, 3 + 3, $-OCH_3$), 5.58 (s, 1, -OH), 6.47 (s, 1, aryl); MS m/e (%) 262 (100.0, M+), 206 (20.2), 205 (78.8).

12,12-Dimethyl-5-hydroxy-4-methoxy-tricyclo[7.3.0.0^{2,7}]-2,4,6-dodecatriene (13).

^{1}H-NMR ($CDCl_3$) δ 0.72 and 1.16 (two s, 3 + 3, gem-dimethyls), 0.9-3.2 (several m, C1-H, C3-H_2, C4-H_2, C5-H_1, C6-H_2), 3.85 (s, 3, OCH_3), 5.50 (s, 1, OH), 6.66 and 6.68 (two s, 2, aryl); MS m/e

(%) 232 (85.7, M+), 176 (27.0), 175 (100.0), 162 (12.6), 161 (10.3), 147 (12.6).

12,12-Dimethyl-5-hydroxy-6-methoxyl-tricyclo[7.3.0.0^{2,7}]-2,4,6-dodecatriene (14).

^{1}H-NMR ($CDCl_3$) δ 0.70 and 1.14 (two s, 3 + 3, gem-dimethyls), 0.9-3.3 (several m, C1-H, C3-H_2, C4-H_2, C5-H_2), 3.85 (s, 3, OCH_3), 5.50 (s, 1, OH), 6.76 (s, 2, aryl); MS m/e (%) 232 (100.0, M+), 176 (30.2), 175 (91.7), 162 (14.3), 131 (11.7), 115 (13.8).

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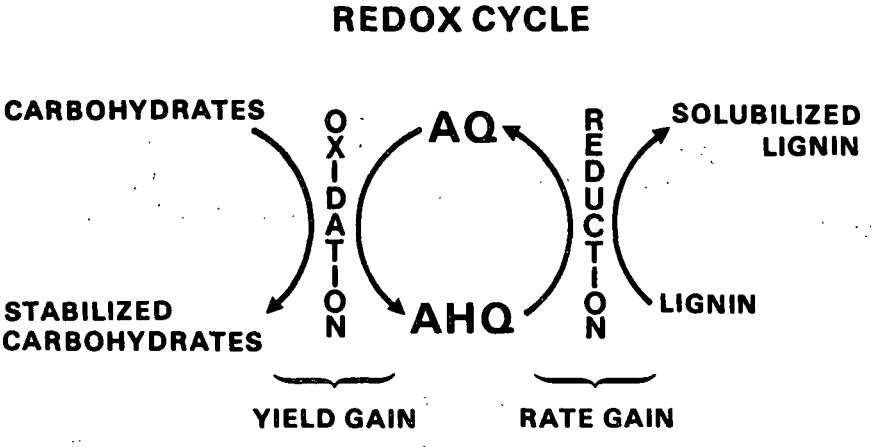
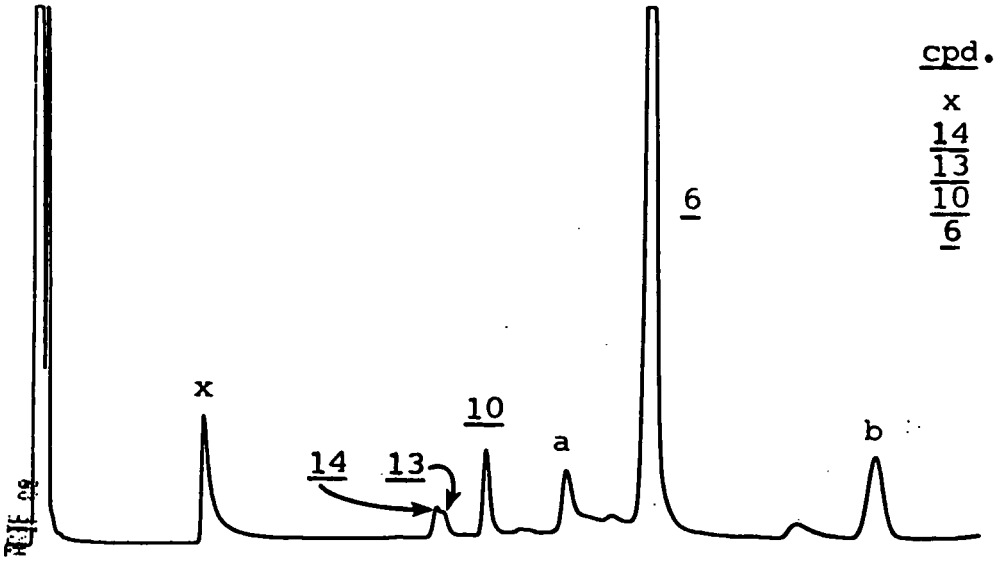
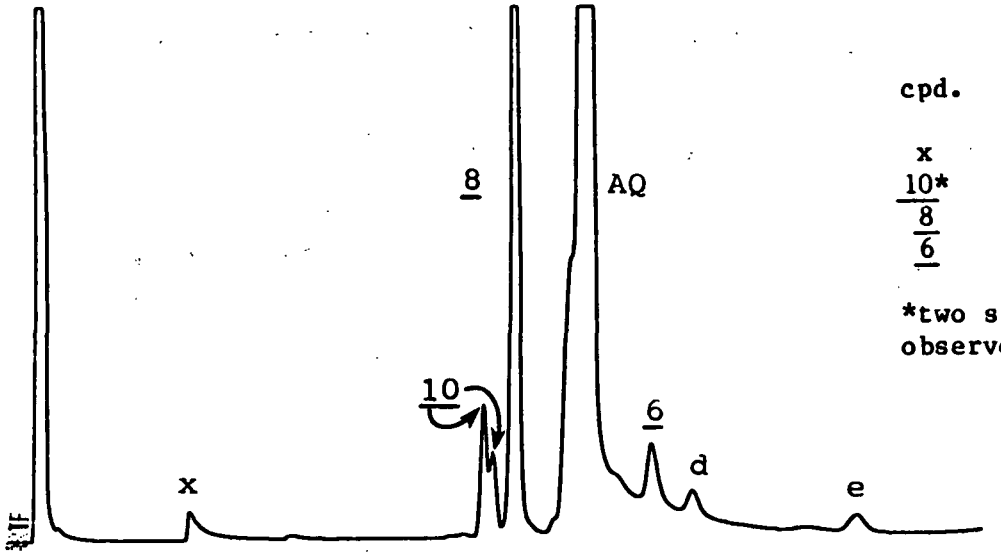


Figure 1. The proposed redox cycle mechanism by which anthraquinone aids wood pulping.

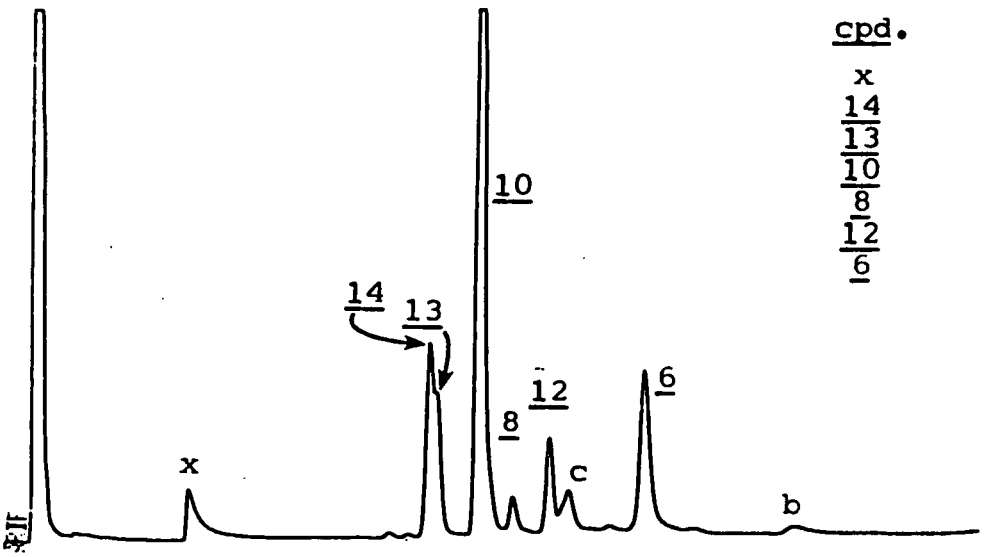


cpd.	area%
x	10.78
14	1.84
13	1.82
10	5.99
6	79.58



cpd.	area%
x	6.62
10*	9.73
8	76.10
6	7.55

*two stereoisomers observed

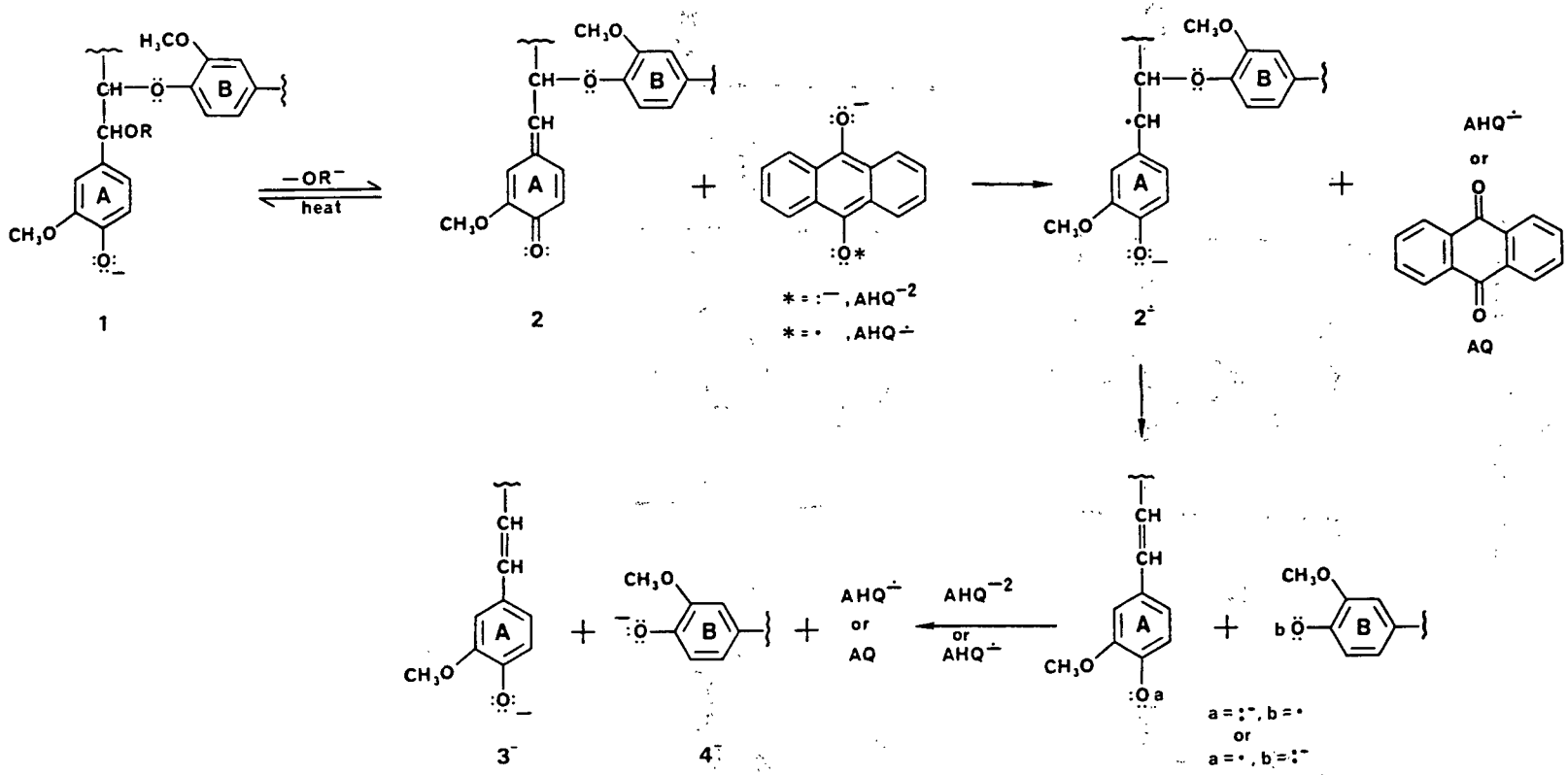


cpd.	area%
x	5.45
14	10.50
13	7.68
10	56.35
8	1.98
12	5.39
6	12.64

Figure 2. The GC chromatograms of the reaction mixtures when **6** was reacted at 135°C with (A) 1M NaOH for 18 hours, (B) 2 molar equivalents of AHQ in 1M NaOH for 2 hours, and (C) 5 molar equivalents of glucose in 1M NaOH for 18 hours. The numbers refer to text structures, x = syringol and a-e unidentified products of apparent molecular weight of 262, 280, 264, 280, and 280, respectively.

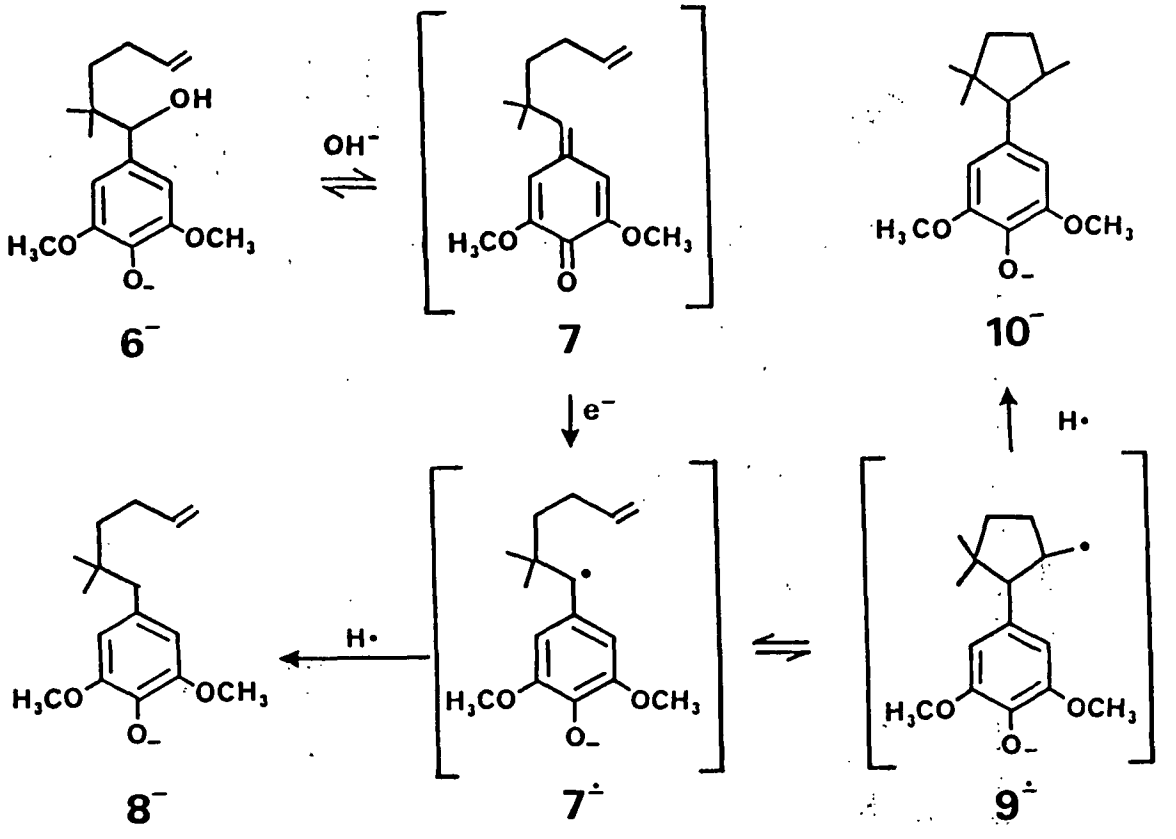
Scheme 1

Delignification via AHQ⁻-induced SET Reactions



Scheme 2

Reactions of Compound 6



Scheme 3

Formation of Additional Cyclization Products